FDD FILE COPY

CLASSIFICATION ~~RESTRICTED~~

CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

FOR OFFICIAL USE ONLY

REPORT

CD NO.

STAT

COUNTRY	USSR	
SUBJECT	Scientific research	
HOW PUBLISHED	Periodicals	
WHERE PUBLISHED	USSR	
DATE PUBLISHED	1945-1947	
LANGUAGE	Russian	

UNCLASSIFIED
JAN 25 1955 /FDD
FOR OFFICIAL USE ONLY

DATE OF INFORMATION   1945-1947

DATE DIST. 19 January 1949

NO. OF PAGES   7

SUPPLEMENT TO REPORT NO.

THIS IS UNEVALUATED INFORMATION

SOURCE   Documentary as indicated. (Information requested.)

RECENTLY PUBLISHED RESEARCH OF THE STATE INSTITUTE OF NITROGEN INDUSTRY, MOSCOW

"Catalytic Oxidation of Hydrogen in the Presence of Manganese Dioxide," L. Glukhovskaya, B. Bruns, State Inst of Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 19, 1945, pp 262-5

An H-O mixture is recirculated over MnO_2 previously heated for several hours at 200-300°; the exact temperature is irrelevant. The yield of H_2O is immeasurably small below 100°. At 125° and 150° the activity of the catalyst decreases during an experiment to about 0.6 of the original activity. At 175° its activity is constant; the rate of reaction is independent of the pressure of O (37-300 mm of dibutyl phthalate) and roughly proportional to the H pressure (75-300 mm of dibutyl phthalate). The reaction constant at 300° is 36 times that at 175°, and the energy of activation is 14,300 calories per molecule. These results are compared with those on the oxidation of CO.

"Thermodynamic Properties of Compressed Nitrogen-Hydrogen Mixtures," I. R. Krichevskiy, Ya. S. Kasarnovskiy, G. T. Levchenko, State Inst of Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 19, 1945, pp 314-22

Literature data are used to calculate the heat capacity, heat content, entropy, internal energy, free energy, etc., of the mixture $N_2 + 3H_2$ between -50° and 200° and between 50 and 1,000 atmospheres.

- 1 -

FOR OFFICIAL USE ONLY

CLASSIFICATION

STATE	X	NAVY	X	NSRB		DISTRIBUTION						
ARMY	X	AIR	X	FBI								

"Method of Deviation Coefficients in the Technical Thermodynamics of High Pressures," A. M. Rozen, State Inst of Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 19, 1945, pp 469-84

Calculation of thermodynamic quantities of real gases is facilitated by using "deviation coefficients," e.g., $T(dP/dT)/P$, $P(dv/dT)/R$, and $P^2(dv/dP)/RT$. All these magnitudes are equal to 1 or -1 for perfect gases but vary for real ones. Tables of these coefficients are given for N_2 between -70° and 500° and between 90 and 6,000 atmospheres, for CO between -70° and 1,000° and 50-1,200 atmospheres, for CH_4 at 0° and 150° between 10 and 1,000 atmospheres, for H_2 between -75° and 200° and 25 and 1,000 atmospheres; and for the mixture $N_2 + 3H_2$ between -50° and 200° and 50 and 1,000 atmospheres.

"Partial Molal Volume, Fugacity, and Activity Coefficients of Nitrogen and Hydrogen in Their Mixture at High Pressures," P. E. Bolshakov, State Inst of Nitrogen Industry, Moscow

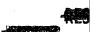"Acta Physicochimica URSS" Vol 20, 1945, pp 259-67

Molal volume, fugacity, and activity coefficients were calculated from available P-V-T data at pressures up to 1,000 atmospheres and temperature 0°-200°. Results are tabulated. The Lewis-Randall rule for fugacities holds well at 200°.

"Partial Molal Volumes of Gases Dissolved in Liquids (Thermodynamics of Dilute Solutions of Nonelectrolytes)," I. R. Krichevskiy, A. Il'inskaya, State Inst of Nitrogen Industry, Moscow

"Acta Physicochimica URSS" Vol 20, 1945, pp 327-48

The comparison of values for the partial molal volume of a gas dissolved in a liquid, determined experimentally and calculated on the assumption that Henry's law holds exactly true in the region of finite concentrations, served as a very sensitive expedient for discovering deviations from Henry's law, even in extremely dilute solutions. In this connection the partial molal volumes of $H_2, N_2, O_2, CO_2, CH_4$, and CO dissolved in H_2O and CH_3OH were measured by a dilatometric method. The measurements were performed at atmospheric pressure and at 0°, 25°, and 50°. The difference in values of the partial molal volumes, determined experimentally and calculated by the equation of Kritchovsky and Kasarnovsky is so great that in no case could it be ascribed to errors in the experimental determination (2-4%) or to inaccuracy in calculating partial molal volumes from the data on solubility. To explain the above difference, the concentration dependence of partial molal volumes and heat contents of solvent and solute for dilute binary solutions were analyzed, and by means of Planck's method expressions for the fugacities of solvent and solute were derived. An equation was

- 2 -

derived for the solubility of a pure poorly soluble
gas in a liquid under pressure, explaining the dif-
ference in values of the partial molal volumes of
dissolved gas, determined experimentally and calculated
by the equation of Kritchevsky and Kasarnovsky. The
empirical character of the latter equation is shown,
although this equation expresses very well the data
on solubility of gases in liquids under pressure.
Analysis of the concentration dependence of the
partial molal volumes and heat contents was applied
to a three-component system, and expressions were
derived for the fugacities of the solvent and two
solutes. Equations were given for the similtaneous
solubility in liquids under pressure of two poorly
soluble gases from their mixtures. It is also explained
why the equation of Kritchevsky and Kasarnovsky,
expresses adequately data of the simultaneous solu-
bility in water under pressure at 25° of H_2 and N_2
from a mixture of them. A diagram of the apparatus
and 48 references are given.

"Solution of Copper in Nitric Acid," A. I. Krasil'-
shchikov and I. V. Dedova, State Inst of Nitrogen
Industry, Moscow

"Zhur Obshch Khimii" Vol 16, 1946, pp 537-42

The process of solution of Cu and HNO_3 was studied.
The rate of solution rapidly rises with increased
temperature and HNO_3 concentration (results are
given graphically). It suggested that either
Cu ions or HNO_2 may act as autocatalysts in the
solution process. It is also proposed that, in
view of the very high temperature coefficient, the
over-all solution is a function of minute electro-
chemical reactions on the surface of Cu, involving
local potential differences which account for the
high order of temperature dependence.

"Remarks on the Formation of Liesegang Rings," A. I.
Krasil'shchikov, State Inst of Nitrogen Industry,
Moscow

"Zhur Obshch Khimii" Vol 16, 1946, pp 1359-62

Resolution of contradictions involved in Ostwald's
classic theory may lie in taking into account the
relation between diffusion and activity. In a binary
system, the diffusion coefficient of a solute is
$D = D_0 \left/\overline{1 + (d\ln f/d\ln c)}\right.$ where $D_0 =$ limiting diffusion
coefficient for indefinite dilution, $f =$ activity
coefficient, $c =$ concentration. Hence, with increas-
ing c, D need not as a rule increase but may under
certain circumstances even decrease. This may lead to
understanding such anomalies as the formation of a
second set of $K_2Cr_2O_7 + AgNO_3$ precipitation rings
after a first set of rings has been formed in a gel.

"Action of Inorganic Acids on Iron: II," A. I. Krasil'-
shchikov, State Inst of Nitrogen Industry, Moscow

"Zhur Obshch Khimii" Vol 16, 1946, pp 1363-8

At 25° after 30, 60, 90, 120, 240, 360 minutes, the
losses of weight of Fe, in g/sq m, in 0.51 liquid
were: in 0.2 N HNO_3, 46.6, 90.1, 104.0, 209.0,
315.0, in 0.5 N HNO_3, 118.9, 254.2, 271.7, 313.2,
378.0, 485.0; in 1.0 N HNO_3, 354.4, 526.9, 693.6,
670.1, 714.9, and 1034.1, respectively. In N HNO_3
after 7 hours, H_2 evolved was but 1.5% of the
theoretical amount; thus solution of Fe in HNO_3
results mainly in the reduction of HNO_3. There
is no indication of any induction period. The
corresponding figures in 2 N H_2SO_4 were 6.36,
9.30, 9.96, 16.92, 25.42, 37.06, and in 0.5 N
HCl 0.97, 1.14, 1.56, 2.99, 2.96, 4.06, respec-
tively. In HNO_3, the loss of weight depends on
the number of samples immersed, examples, 7 hours,
HNO_3 0.1, 0.2, 0.5, 1.0 N, 3 samples 8.84-10.62,
17.87-20.73, 34.12-53.08, 93.07-102.10, one sample
27.38, 51.80, 101.35, 313.08 g/sq m. The rate of
solution in HNO_3 is approximately a linear
function of concentration, example, 7 hours at 25°,
0.01, 0.03, 0.07, 0.10, 0.30, 0.60, 1.00 N, mean
of 3 samples: 1.26, 2.98, 6.92, 9.93, 28.13,
49.24, 96.49 g/sq m/hr. In the passive region,
the rate falls with increasing concentration,
example, 8,10,14,16,18,21 N, loss of weight 8.00,
5.52,2.72,1.80,1.23,0.86 g/sq m/hr. In 16,18,21
N HNO_3, the rate of solution at 60° is 15-20 times
that at 25°; thus the temperature is determined by
chemical, not by diffusion processes, in contrast
to solution in the active region.

"Anomalous Phase Transitions," I. R. Krichevskiy,
A. M. Rozen, State Inst of Nitrogen Industry,
Moscow

"Zhur Fiz Khimii" Vol 20, 1946, pp 935-40

Mayer's theory of anomalous phase transitions of the
first order contradicts thermodynamics. If the
theory is altered to reconcile it with thermodynamics,
no difference remains between the anomalous and
normal phase transitions.

"Solubilities of Nitrogen and Carbon Dioxide in
Methanol Under Pressure," I. R. Krichevskiy,
E. S. Lebadeva, State Inst of Nitrogen Industry,
Moscow

"Zhur Obshch Khimii" Vol 21, 1947, pp 715-18

The solubility of N_2(cc N T P in 1 g) at 0° is
7.7 and 28.5 at 48.4 and 194 atmospheres, respectively,
and at 75° is 9.3 and 51.6 at 48.4 and 280 atmospheres,
respectively. The solubility of CO_2 at 0° is 59.5
and 270 at 6.8 and 22.3 atmospheres, respectively,
and at 75° is 12.8 and 234 at 6.8 and 68.8 atmospheres,
respectively. Many intermediate values are given

- 4 -

also. The results agree well with the determinations by Just, "Zhur Fiz Khimii" Vol 37, 1901, pp 342, but are higher than those of some recent investigators.

"The System Iron-Nitrogen at High Pressures,"
I. R. Krichevskiy, N. E. Khazanova, State Inst
of Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 21, 1947, pp 719-33

It is shown by calculation and experiment that Fe nitrides have a lower vapor pressure of N_2 and are capable of existing at lower N_2 pressures than hitherto believed. The older calculations failed because they assumed the laws of perfect gases to be valid at extremely high pressures and the activity of the solid phase and the equilibrium diagram of the solid to be independent of pressure. When these assumptions are not made, the following equilibrium pressures (in atmospheres) of N_2 are found: α phase $+ \gamma +$ phase $+ N_2$, 2,100 at 300° and 2,700 at 500°; $\alpha + \gamma + N_2$, 3,200 at 550°, and 2,450 at 650°; $\gamma + \gamma' + N_2$, 3,100 at 550°, and 3,650 at 591°; and $\alpha + \gamma + \gamma'$, 4,000 at 550° and 1 (metastable) at 591°. The quaternary point $\alpha + \gamma + \gamma' + N_2$ is at 550° and 3,100 atmospheres. These results were tested by heating Fe, pure or containing 5.6% of Al_2O_3 and 1.4% of K_2O, prepared from Fe_4N, in N_2 at 350-525° and 750-3,800 atmospheres. The concentration of N in the solid phase obtained varied irregularly so that no definite effect of pressure or of duration of heating could be detected. Previous "charging" of the solid with O_2 increased the N content up to 3.1%. It is not known why nitriding stopped before reaching equilibrium. In agreement with calculation, the γ' phase is present (x-rays) at 475° at 2,690 atmospheres, but only the γ phase is found at 2,270 atmospheres. The lattice spacing of the γ phase showed that it was saturated with N.

"Air Depolarization of a Nickel Cathode," A. I. Krasil'shchikov, State Inst of Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 21, 1947, pp 849-54

Curves of cathodic polarization of Ni in slightly acid solutions (0.1 M K_2SO_4 + 0.002 N H_2SO_4) saturated with air show two horizontal sections (along which the current density is independent of applied voltage). The first section is due to diffusion of O and occurs at current density of $1 - 2 \times 10^{-5}$ amp/sq cm. The second section is caused by catalytic liberation of H. Slightly alkaline solutions exhibit only the first section at a current density which is the same for stainless steel and Fe. This constant current density is determined by the rate of diffusion of O. Neutral solutions (0.1 M K_2SO_4) give rise either to curves similar to those in alkaline solutions or to nearly straight lines on which no depolarization by air is detectable.

- 5 -

STAT

"Study of a Silver Cathode in the Presence of Dissolved
Oxygen." I. P. [illegible], A. I. Krasil'shchikov,
State Inst of Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 21, 1947, pp 855-62

The curves of cathodic polarization of Ag in 0.1
M K_2SO_4, KCl, or NaOH or in mixtures of 0.1 N
K_2SO_4 and dilute NaOH, all saturated with air, are
nearly coincident and almost reversible. This reversi-
bility demonstrates the corrosion stability of Ag.
The curves consist of three branches, the increase
of current density with applied voltage is much less
steep along the second than along the first and the
third branch. In acid solutions, e.g., 0.1 M
K_2SO_4 + 0.015 N H_2SO_4, there are two steep and two
almost horizontal branches. If 0.1 M K_2SO_4 solution
is saturated with O instead of air, the polarization
curves become similar to those observed in stirred
solutions saturated with air. The anodic polari-
zation curves are different for different solutions.
The rise of current density with voltage is
greatest in 0.1 M KCl, smaller in 0.1 M K_2SO_4,
and smallest in 0.1 M NaOH, all saturated with
air.

"Catalysis in Stages," B. P. Bruns, State Inst of
Nitrogen Industry, Moscow

"Zhur Fiz Khimii" Vol 21, 1947, pp 1011-18

If the reaction between two gases, A and B, can be
accelerated by a catalyst when the catalyst is brought
in contact with first A alone and then B alone, the
catalysis occurs in stages. Catalysis in stages
is impossible if the catalyst is chemically altered
during catalysis, e.g., MnO_2 is reduced to Mn_2O_3 when
it accelerates the reaction between CO and O_2. The
hydrogenation of ethylene in the presence of Pt
cannot be realized in stages, because the metal
surface contains two types of regions, one of
which is blocked by the absorbed gas. The chemical
change of a catalyst during its work should
be borne in mind when comparing the activity with
the composition of catalysts.

"Kinetics of Ammonia Synthesis in Isothermal Conditions,"
L. P. Sidorov, V. D. Livshits, State Inst of Nitrogen
Industry, Moscow

"Zhur Fiz Khimii" Vol 21, 1947, pp 1177-81

The equation of Temkin and Pyzhev is valid for the
synthesis of NH_3 at 300 atmospheres between 425 and
525°, when the rate of flow of outgoing gas varies
from 15,000 to 150,000 times the volume of catalyst
per hour. The catalyst was Fe promoted with Al_2O_3
and K_2O. The laboratory apparatus used, suitable
also for studying other exothermal processes at
high pressures at a constant temperature, is described.

STAT

"Anomalous Phase Transitions. Behavior of Sub-
stances Near Their Critical Points," I. Krichevskiy,
A. Rozen, State Inst of Nitrogen Industry, Moscow

"Acta Physicochimica URSS" Vol 22, 1947, pp 153-61

"Zhur Fiz Khimii" Vol 20, 1946, pp 935-40

Mayer's theory of anomalous phase transitions of the
first order contradicts thermodynamics. If the
theory is altered to reconcile it with thermodynamics,
no difference remains between the anomalous and
normal phase transitions.

- E N D -